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US Army Research Laboratory

Mechanical and Impact Characterization of Poly-Dicyclopentadiene (p-DCPD) Matrix Composites Using Novel Glass Fibers and Sizings

by Steven E Boyd

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14. ABSTRACT
A survey of mechanical and impact properties for glass-reinforced polydicyclopentadiene (p-DCPD) matrix composites is undertaken to assess the suitability of the new resin system as a replacement for existing epoxy-matrix systems. The p-DCPD resin system has superior thermal stability and intrinsic fracture-toughness properties that are desirable for Army-unique applications. However, challenges in conventional processing techniques and chemical-sizing compatibility were encountered during the study. Various novel glass fibers and commercially available fabrics were infused with both p-DCPD resin and SC-15 epoxy and mechanical and impact testing performed. The key results indicate p-DCPD composites have lower mechanical and impact performance compared to SC-15 composites due to chemical-sizing incompatibility at the fiber–matrix interface. Despite efforts to tweak processing and to develop compatible sizings with industry partner Pittsburgh Plate Glass Industries, the p-DCPD composites had poor interfacial bonding that manifested as significantly lower interlaminar-shear strength. The main conclusion of this study is this: Given the desirable properties of p-DCPD, a program effort should be undertaken to develop a chemical sizing that will be 100% compatible with the p-DCPD resin and allow for processing of composites that have improved or comparable structural—as well as ballistic—properties to epoxy-matrix composites.

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1. Introduction

Whether used as a neat resin or as a matrix material in a fiber-reinforced composite, epoxy-resin systems have been successfully used in industrial and military applications for decades. Some important limitations of epoxy composites compared to more traditional monolithic materials include relatively brittle properties (lower impact strength, damage tolerance, elongation to failure, and delamination) and moderate hot/wet glass transition temperature (*Tg*; ~95°C/85°C). Poly-dicyclopentadiene (p-DCPD), an aliphatic hydrocarbon resin, has superior impact properties and toughness, a high hot/wet *Tg* (>124°C), and good mechanical properties compared with epoxies.[1] This set of desirable properties, especially the thermal stability, high intrinsic toughness, and resistance to delamination, make the investigation of p-DCPD resin as a potential matrix material very relevant to Army-unique applications.

Poly-DCPD is formed by a process known as ring-opening metathesis polymerization (ROMP).[2] Older catalysts for the ROMP reaction include molybdenum and tungsten and are known to be susceptible to moisture, air, and other chemicals. The newer ruthenium (Ru)-based catalysts are much less sensitive and may be used in vacuum-assisted resin transfer molding (VARTM) in the fabrication of composites.

There are a number of challenges that had to be addressed or overcome to manufacture viable p-DCPD composites for testing. By far the largest impediment was finding a good coupling agent (sizing) to create a good bond between the fiber and this aliphatic hydrocarbon resin; industry-standard amino silane sizings were chemically incompatible or failed to create a good bond. Through a congressional program[3] the Army has with Pittsburgh Plate Glass (PPG) Industries, PPG—which also was tasked with developing a new glass fiber—developed over the course of its work 3 proprietary sizings that are featured in this report and showed some progress toward improving the fiber–matrix bond. Another major issue was the sourcing of the resin system: Previous composite samples were manufactured by Materia, Inc., and performed well[4]; however, Materia would not supply us with resin or catalyst. Therefore, resin was sourced from Spencer Composites,[5] which provided an Ru-catalyst–p-DCPD-resin system known as ESM-611+. A final hurdle was resin pot life and viscosity. The ESM-611+ resin system we sourced had sufficient pot life to infuse a large composite panel or structure (in contrast to many p-DCPD resins, which gel in seconds or minutes) but had a very low viscosity of approximately 20 centipoise (cP) at room temperature, making resin retention in

the part under vacuum difficult. As a result the standard VARTM process was modified and yielded good panels without dry voids or resin-starved composites.

This report focuses on mechanical and low-velocity-impact characterization of various glass-fiber-reinforced p-DCPD matrix composites. The composites tested may seem disparate but represent what was manufactured considering the challenges already discussed. Whenever possible, a companion composite featuring the same fiber architecture and sizing was manufactured using a 2-phase, toughened epoxy resin system by Applied Poleramic Inc.,[6] and tested for comparison. Though 2-D, 24-oz woven roving fabrics are of most interest, satin weaves were acquired and tested based on the recommendation of Brian Spencer of Spencer Composites, from which we sourced the p-DCPD resin. One p-DCPD composite uses a proprietary p-DCPD formulation provided by Telene SAS[7] directly to PPG. This panel was made by US Army Research Laboratory (ARL) technicians J Wolbert and M Thompson at PPG in Shelby, North Carolina, and provided for testing. Due to limited amounts of both glass fabric and resin, only tension, flexural, and short beam shear (SBS) testing was conducted; further, impact testing was conducted on only 5 composites.

2. Materials

2.1 Fibers and Fabrics

The fabric reinforcements used in this study are listed in Table 1. Four 24-oz, 5 × 5 woven rovings were used: 3 were supplied by PPG (E-glass, X1-glass, and X2-glass) and one from Advanced Glassfiber Yarns (AGY),[8] S2-glass. The X1- and X2-glass fibers are experimental fibers developed as a key goal of the PPG congressional program.[3] They were of higher strength and elongation than the industry-standard E-glass and were comparable in properties to the S2-glass fiber. These fibers were woven at PPG into fabrics and supplied to ARL in rolls. The AGY fabric is a 24-oz, 5 × 5 woven roving of S2-glass fiber that is also provided as a 50-inch-wide roll.

Table 1 Material constituents and sizings for composites used in the current study

Fabric/fiber	Fiber sizing	Polymer matrix
JPS Glass 6781 S2-glass 8-h satin weave	JPS 9827 (Amino Silane)	Both SC-15 and p-DCPD
Hexcel 7781 E-glass 8-h satin weave	Amino-Silane	Both SC-15 and p-DCPD
AGY S2-glass 24-oz woven roving	AGY 933	Both SC-15 and p-DCPD
PPG E-glass 24-oz woven roving (washed)	PPG 1383	Both SC-15 and p-DCPD
PPG X1-glass 24-oz woven roving (washed and unwashed)	PPG 1383	p-DCPD only
PPG X2-glass 24-oz woven roving	PPG T-74	p-DCPD (ESM-611+ and PPG Telene)
PPG E-glass biaxial stitched	PPG 2026	Both SC-15 and p-DCPD

Two satin weaves were also used in this study: the E-glass 8-harness Hexcel 7781[9] and the S2-glass, 8-harness 6781 from JPS Glass.[10] These 2 fabrics were incorporated into the study after consultation with Brian Spencer. Spencer Composites has manufactured panels using the satin weave fabrics and its proprietary p-DCPD resin, ESM 611+. Toward the end of the study, ARL requested PPG provide us with a fabric sized with PPG 2026 sizing. ARL received a biaxial, stitched E-glass fabric roughly equivalent in areal weight to the 24-oz woven roving materials.

2.1.1 Resin Systems

The resin systems (and fiber sizings) used are also listed in Table 1. Where possible, the composites tested were manufactured using both p-DCPD and an epoxy for direct comparison. The standard epoxy-resin system used at ARL is a 2-phase, toughened epoxy, SC-15, manufactured by Applied Poleramic Inc.[6] The p-DCPD resin system from Spencer Composites,[5] ESM-611+, is an Ru-catalyst system. Composites using Telene[7] p-DCPD were manufactured exclusively at PPG and provided to ARL as large panels and also use a Ru-based catalyst. The ESM-611+ was purchased by ARL for its exclusive use courtesy of Spencer Composites. The Telene p-DCPD resin system was specially developed for use by PPG with its experimental-fibers program and was not provided to ARL; however, PPG manufactured panels to ARL specifications that were tested at ARL "as received".

2.1.2 Fiber Sizings

There are a number of fiber sizings used in this study on the various glass fibers. Most of the sizings are compatible with epoxy-matrix chemistry and are proprietary to the fabric manufacturers. The sizings on the 2 satin weave materials are amino-silane type. The AGY sizing is a Type 933 inorganic, high-temperature sizing. The 2 sizings applied to PPG fabrics supplied to ARL, 1383 and 2026, are understood

to be compatible with epoxy-matrix chemistry. It is important to note here the explanation of "washed" versus "unwashed" in Table 1. An attempt was made to remove the fiber film former (a polyester) and the amine type sizing (1383), which is known to be incompatible with p-DCPD, using an acetone wash. After interaction with and recommendations from ARL, PPG developed the Type T-74 sizing (one of 3), which is an attempt to render the sizing more compatible with the unique chemistry of p-DCPD resin.

2.2 Manufacturing of Composites

All composites in this study were manufactured using vacuum-assisted resin transfer molding (VARTM). Depending on the resin system, the standard VARTM procedure had to be modified to produce a viable part. The 2 alterations of standard VARTM used in this study are low-viscosity resin VARTM and press-assisted VARTM (PA-VARTM).[11]

Standard VARTM procedures include laying up a part on a nonreactive, impermeable surface (a "tool" surface such as glass or metal caul plate), bagging the part—allowing for an inlet for resin and outlet for vacuum—and compacting the setup under vacuum and infusing the part (fabric lay-up) with resin. The standard VARTM procedure works well with resin systems that have a viscosity between 200 and 5000 cP and a pot life of at least 20 min. The chosen epoxy system, SC-15, infused quite well with this technique and produced good, low-void-content composite parts. SC-15 resin was infused and cured until gelled at 60 °C (140 °F) and then post-cured at 121 °C (250 °F) for at least 4 h.

The p-DCPD resin system has a very low viscosity of less than 20 cP (versus 300 cP of SC-15).[6] For a standard VARTM setup, if the viscosity of the infused resin is too low, the vacuum will quickly draw off the resin through the outlet leaving the fabric resin-starved, even if the outlet is sealed with clamping pliers. To mitigate this, a special low-viscosity VARTM procedure was developed by ARL's Wolbert to increase infusion time, reduce vacuum pull, and contain the p-DCPD resin once it infused the part. Figure 1 shows 2 images of the modified setup. Not pictured are the screw compressor clamps that served as a fine adjust to reduce the resin-flow volume at the inlet and cut off vacuum pull at the outlet, both in an effort to increase infusion time. The addition of a metal window-frame resin barrier or "reservoir" was added to enclose the part to contain the resin and make it more difficult for the vacuum to siphon off. The reservoir barrier was placed around the part and was very successful along with the secondary bag at containing the p-DCPD resin. It was eventually made to manufacture 12-inch × 12-inch × 0.25-inch (30.5-cm × 30.5-cm × 0.64-cm) panels and thicker 16-inch × 16-inch × 0.5-inch

(40.6-cm × 40.6-cm × 1.3-cm) panels. One final difference noted in Fig. 1 is the use of only peel-ply cloth to lead from part to outlet, which is noticeably set back again in an effort to slow the vacuum pull on the resin.

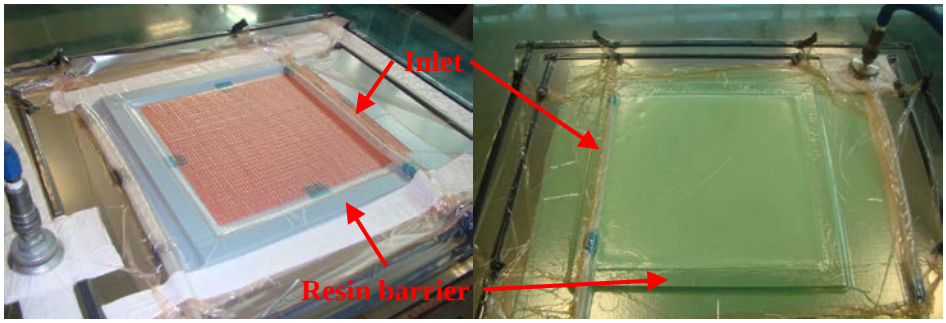

Fig. 1 The low-viscosity VARTM set-up used to manufacture p-DCPD composites tested in this study

Despite these efforts, resin infusion took only a minute using the ESM-611+ p-DCPD resin after which primary (inner) bag vacuum was closed with the compressor clamp. The part was left overnight to gel and then post-cured at 121 °C (250 °F) for 4 h. Composites made with p-DCPD were noted for the pungent residual odor indicating unreacted polymer. Eventually the cure and post-cure procedure were changed to increase the degree of cross-linking in the resin. The new cure cycle comprised a temperature hold at 60 °C (140 °F) until gel; a 4-h post-cure to 121 °C (250 °F); and a final post-cure of 177 °C (350 °F) for 2 h. The new cure cycle yielded composites that have reduced residual odor, but did not completely eliminate it.

Composites containing the Telene p-DCPD proprietary resin system were manufactured at PPG's Shelby, North Carolina, facility by ARL personnel in a single trip using a hybrid method incorporating elements of low-viscosity VARTM. The cure and post-cure of the Telene p-DCPD panels was the same as that used at ARL. No additional post-cure or processing was completed after the panels were received by ARL and they were tested "as received".

2.3 Fiber Burn-out Results

Once the p-DCPD composite panels were manufactured, small samples were taken from the unused fringes for fiber burn-out testing. Three to 4 samples of each panel measuring 1-inch square were weighed dry and wet and then heated in a crucible to 565 °C to burn off the polymer matrix. The remaining glass fibers plus crucible were weighed to determine the residual glass weight. Table 2 reports the composite volume fractions for the fibers (V_f), matrix (V_m), and voids (V_v), all of which were calculated according to American Society for Testing and Materials (ASTM)

International standards D792 and D2734.[12,13] The results are for the composite panels tested for mechanical properties. According to Table 2, the modified VARTM process was largely successful in manufacturing panels with low void content; however, a few panels (highlighted in yellow) had higher void fractions than desired.

Table 2 Volume fractions for p-DCPD composites used in the mechanical testing

Composite	Panel ID	V_f (%)	V_m (%)	V (%)
6781–SC-15	4019	48.0	50.0	2.0
6781–p-DCPD	3099	46.4	50.7	3.5
7781–SC-15	3073	48.7	50.6	0.7
7781–p-DCPD	4029	46.3	52.7	1.1
X1 (not washed)–p-DCPD	4094	55.4	42.6	2.0
X1 (washed)–p-DCPD	5014	57.0	34.8	5.7
E (washed)–SC-15	5001	55.4	44.2	0.4
E (washed)–p-DCPD	4095	52.9	46.3	0.8
S2-933–SC-15	5004	47.8	51.5	0.7
S2-933–p-DCPD	5012	41.0	48.6	7.6
E (Biaxial)–SC-15	5126	59.5	40.0	0.5
E (Biaxial)–p-DCPD	5124	58.1	40.8	1.1
X2–p-DCPD	5170	39.2	59.0	1.8
X2–PPG Telene p-DCPD	PPG no.4	43.0	~55.0	~2.0

Fiber burn-outs were also conducted on the composite panels used in the impact study and results are presented in Table 3. Yellow highlights the composite with the highest void fraction.

Table 3 Fiber burn-out results for p-DCPD composites used in impact testing

Composite	Panel ID	V_f (%)	V_m (%)	V_v (%)
E–DCPD VARTM	4093	48.4	50.8	0.8
E–SC-15 VARTM	4090	48.9	50.5	0.6
E–DCPD PA VARTM	5029	49.0	47.0	4.0
E–SC-15 PA VARTM	5034	52.2	47.3	0.5
X2–PPG Telene p-DCPD	PPG no. 4	43.0	~55.0	~2.0

The "PA VARTM" description in Table 3 actually refers to a variation of the standard VARTM process in which the glass fiber-layers are compacted by both vacuum bag and by means of a press to increase the fiber-volume fraction. The press-assisted VARTM manufacturing process is discussed in detail by Holmes et al.[11] Again, most of the composite panels were successfully manufactured.

2.4 Mechanical and Impact Testing

All composite panels manufactured for the mechanical testing had finished dimensions of approximately 11 inch × 11 inch × 0.25 inch (28 cm × 28 cm × 0.6 cm). This provided a small panel from which only a few samples could be obtained for a few types of mechanical test. Tension, flexural, and short beam shear

(SBS) testing were selected to provide a measure of interlaminar shear and tensile properties and strengths. The tension and flexural samples were identical at 11 inch × 1 inch × 0.25 inch (28 cm × 2.5 cm × 0.6 cm). The tension samples were tested according to ASTM D3039[14] with strains measured using digital-image correlation (DIC) with a single-camera, 2-D setup. Flexural testing was conducted according to ASTM D790[15] using a recommended 40:1 aspect ratio for the span. SBS testing samples were 1.5 inch × 0.5 inch × 0.25 inch (3.8 cm × 1.2 cm × 0.6 cm) and were tested according to ASTM D2344.[16]

Impact testing was performed on all the composites listed in Table 3 using the ARL-developed 4-quadrant, low-velocity-impact protocol. The method and its development and analysis are discussed in detail by Emerson et al., and Boyd et al.[17–20]; therefore, only a very brief description follows. Impact testing of thick-section composite panels is conducted using a medium-energy Dynatup 8100 drop tower, as shown in Fig. 2. The impact sample's dimensions are 16 inch × 16 inch × 0.5 inch (40.6 cm × 40.6 cm × 1.2 cm) and it was subjected to 4 separate impacts, one in each quadrant.

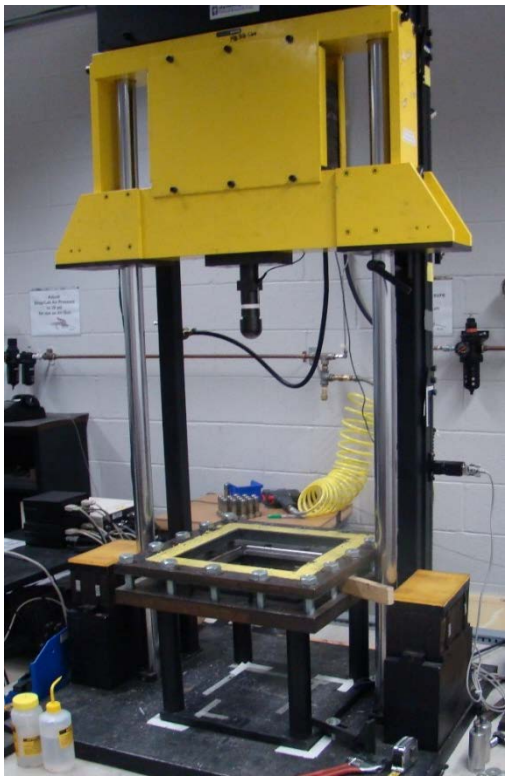

Fig. 2 Dynatup 8100 medium-energy drop tower with impact-table fixture installed

A special fixture called the impact-table fixture was made to hold the sample during

the impact event as shown schematically in Fig. 3. The panel was removed after each impact and ultrasonically scanned to provide a measure of impact-damage progression.

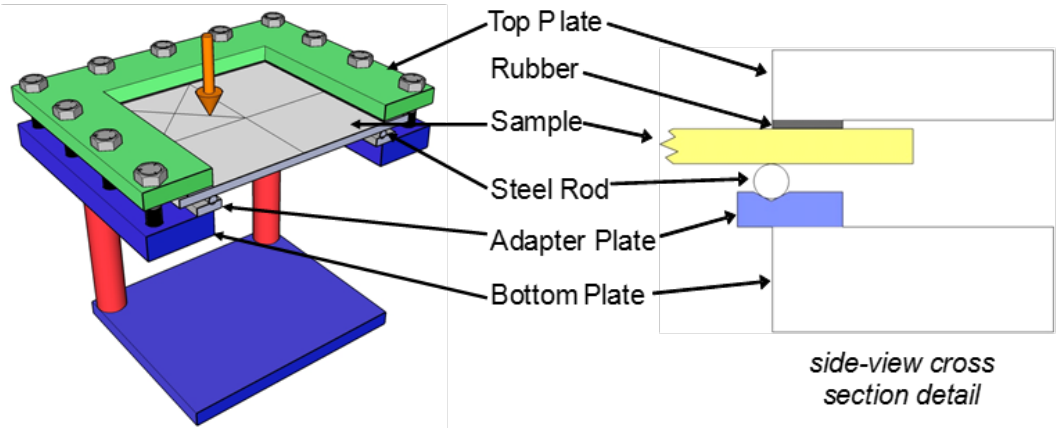

Fig. 3 Schematic drawing of impact-table's fixture supports and location of impact

Once all 4 impacts were completed, a force-deflection curve was constructed and a damage-area progression analysis conducted. Table 4 gives detailed information on the thick-section composite panels tested in impact.

Table 4 Composite samples tested with low-velocity-impact protocol for thickness, weight, and areal density

Fabric	Lay-up	Resin	Thickness (cm)	Weight (g)	Areal density kg/m^2 (lb/ft^2)
2-D, 24-oz E-glass	22-ply woven roving E-glass, quasi-isotropic	Ru-cat/p-DCPD	1.47	4415	26.7 (5.5)
		SC-15 epoxy	1.52	4359	26.4 (5.4)
2-D, 24-oz E-glass, PA-VARTM	22-ply woven roving E-glass, quasi-isotropic	Ru-cat/p-DCPD	1.42	4170	25.2 (5.2)
		SC-15 epoxy	1.24	3943	23.9 (4.9)
2-D, 24-oz X2-glass	22-ply woven roving X2-glass, quasi-isotropic	Proprietary Telene formulation p-DCPD	1.96	5027	30.4 (6.2)

3. Results and Discussion

3.1 Mechanical Testing

3.1.1 SBS Testing

Results of the SBS testing are presented in Table 5. Without exception, the SC-15 resin composites had a higher SBS strength. The SBS strength in p-DCPD composites was poor regardless of fiber architecture or glass fiber. The p-DCPD composite that performed best was the satin-weave 7781 E-glass at 30.6 MPa (only a 35% reduction). It is not known why the 7781 E-glass composite performed well versus the group; the other satin weave, the 6781 S2-glass, performed poorly. It may have something to do with the individual proprietary sizings applied to both fabrics and the 8-harness satin weave architecture under short span, 3-point bending. Both the PPG X1-glass and Bi-axial E-glass composites had single-digit SBS strengths with the PPG E-glass and AGY S2-glass composites having an 11.9- and 10.1-MPa SBS strength, respectively. In regard to the PPG X1-glass, the attempt to remove the film former with an acetone bath—"washing" versus "unwashed"—and improve p-DCPD wetting did not improve SBS strength but, rather, decreased it. The 2 PPG X2-glass composites with the T-74 sizing performed better than the group, but still demonstrated SBS strength values that were less than half of the SC-15 resin composites.

Table 5 Short-beam shear strengths and failure modes of SC-15 and p-DCPD resin composites tested

Fabric	SC-15 (MPa)	Failure	p-DCPD (MPa)	Failure
6781	49.7	Flexure	14.7	. . .
7781	47.5	Flexure	30.6	. . .
PPG E	33.0	Flexure	11.9	. . .
PPG X1	NA	NA	7.5	. . .
AGY S2-933	43.4	Flexure	10.1	. . .
PPG X1 (washed)	NA	NA	7.0	. . .
Biax (2026 PPG)	46.3	Flexure	6.0	. . .
X2(T-74)–PPG Telene	NA	NA	19.0	. . .
X2(T-74)–ESM 611+	NA	NA	17.0	. . .

Visual inspection of the tested samples sometimes reveals the mode of failure. Figure 4 illustrates the failure modes of 3 satin-weave composites for comparison. Table 5 shows all of the SC-15 resin composites failed in flexure, namely compression under the point of load application forming a kink band. The failure is visible in Fig. 4 in the 7781 E-glass (left, top, and bottom) and the 6781 S2-glass (center, top, and bottom) composites. Determination of the failure modes was

difficult for the p-DCPD resin composites. The 6781 S2-glass–p-DCPD resin composite (right, top, and bottom) in Fig. 4 is characteristic of the other p-DCPD composites and is pictured next to the corresponding SC-15 resin composite. The p-DCPD composites demonstrate no discernable kink band or bending-tension failure on the outer fiber layer, but only a slight indent due to the loading nose along with a characteristic bent span seen with most samples tested in 3-point bend. The failure here is most likely interlaminar shear without visible delamination planes. The visual inspection together with the SBS strength data of Table 5 strongly indicate the p-DCPD composites have significantly reduced interlaminar shear strengths, most likely due to chemical incompatibility between the sizing and the p-DCPD resin, which forms a poor fiber–matrix interface during cure.

Fig. 4 Tested SBS samples for visual inspection of failure mode: (left) 7781 E-glass–SC-15, (center) 6781 S2-glass–SC-15, and (right) 6781 S2-glass–p-DCPD

3.1.2 Flexural Testing

Flexural testing was attempted on both SC-15 and p-DCPD resin composites. There were 2 problems while conducting the flexural tests. First, most of the p-DCPD resin composites were not failing prior to the 5% bending-strain limit defined by ASTM D790 despite using a 40:1 ratio. This renders the ASTM D790-test results invalid or, at very least, suspect. Second, given the smaller panel size manufactured and the resulting limited number of 11-inch × 1-inch × 0.25-inch (28-cm × 2.5-cm × 0.6-cm) samples that could be tested, there were not enough samples to provide an acceptable sample size (minimum of 5) for both flexural and tension testing.

Given the higher probability of obtaining good data from tension testing, flexural testing was discontinued.

A complete set of flexural data for the satin-weave composite 6781 S2-glass is presented here to provide a representation. The flexural stiffness of the 6781 S2-glass–SC-15 composite was 23.3-GPa versus 15.6-GPa for the 6781 S2-glass–p-DCPD composite, and the flexural strength was 495-MPa versus 193.4-MPa. The SC-15 resin composite's failure mode was flexure showing compression failure under the load nose and the p-DCPD resin composite; a combination of flexure and interlaminar shear as shown in Fig. 5. Again, the sizing incompatibility appears to have significantly lowered both the flexural stiffness and strength of p-DCPD versus a corresponding SC-15 resin composite.

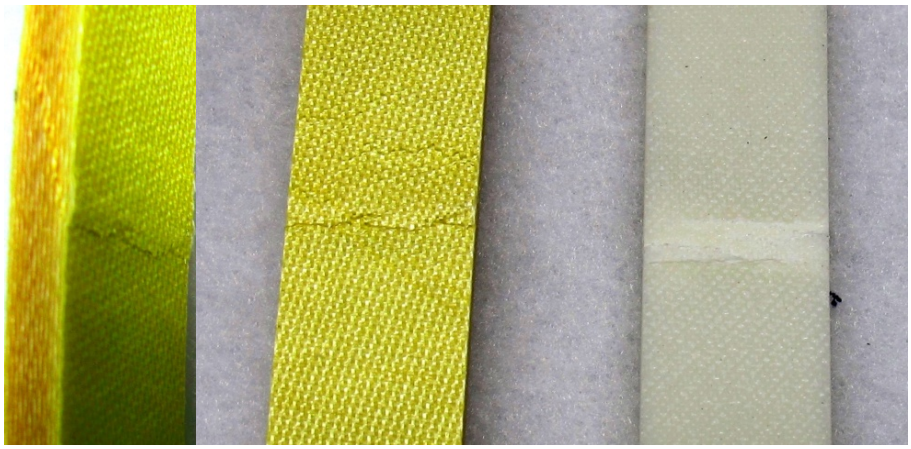

Fig. 5 Tested 3-point-bend flexural samples for visual inspection of failure mode: (left and edge left) 6781 S2-glass–p-DCPD and (right) 6781 S2-glass–SC-15

3.1.3 Tension Testing

Tension testing was completed on all composites listed in Table 2. DIC was used to evaluate the strain field over a gage length of 4–5 inches (about 10–12 cm) and calculate a stress–strain curve for each material. At least 5 replicates were performed for each material. Young's modulus in the linear region (subjectively determined from the stress–strain curves) and the ultimate tensile strength (based on the maximum load obtained) are reported in Table 6. The PPG experimental fibers had no SC-15 resin composite for comparison (as indicated by "NA" in the table) and results are only reported for p-DCPD resin. The lack of an SC-15 composite for these fibers is because ARL received small amounts of fabric from PPG; since these fibers have unique sizings specifically formulated for the Telene p-DCPD resin, it was decided to focus on infusing these fabrics solely with p-DCPD resin. In Table 6 the fiber architectures are divided into satin weaves in the first 2 rows and woven rovings in the remainder.

Table 6 Tension data for SC-15 and p-DCPD composites ("NC": not completed)

Fabric	SC-15		p-DCPD	
	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)
6781	23.4	480.1	19.9	404.4
7781	20.9	344.7	19.5	279.0
PPG E	23.6	350.4	17.4	324.4
PPG X1	NA	NA	15.0	306.5
AGY S2-933	22.6	405.4	NC	NC
PPG X1 (washed)	NA	NA	18.7	324.6
Biaxial (2026 PPG)	27.3	437.7	22.2	393.8
X2(T-74)–PPG Telene	NA	NA	14.1	324.8
X2(T-74)–ESM 611+	NA	NA	15.7	228.3

The satin-weave composites, 6781 S2-glass and the 7781 E-glass, were recommended by Spencer Composites based on its experience with infusing p-DCPD resin. Except for the 6781 S2-glass–p-DCPD composite, all satin weaves had a low void fraction (2.0% or less) and a fiber-volume fraction of 46%–49% (Table 2). The 6781 S2-glass composites are stiffer and stronger than the 7781 E-glass composites due to the difference between the glass fibers. There is a noticeable drop off in strength of about 20% between the p-DCPD matrix and SC-15 matrix composites. The moduli values are, however, very similar, although there is a discernable decrease in the p-DCPD composite stiffness. Even though tension tests are fiber dominated, the fiber–matrix bond and shear strength do influence the results. Visual inspection of the failed coupons (illustrated in Fig. 6) explains why there is an observed drop off in tensile strength with the p-DCPD composites. Figure 6 has 2 images each of the 6781 S2-glass–p-DCPD (left) and 6781 S2-glass–SC-15 (right). The SC-15 resin composite has a clean break in the gage length with no interlaminar delaminations. The p-DCPD resin composite suffers multiple axial delaminations, which erode stiffness and result in lower strength values.

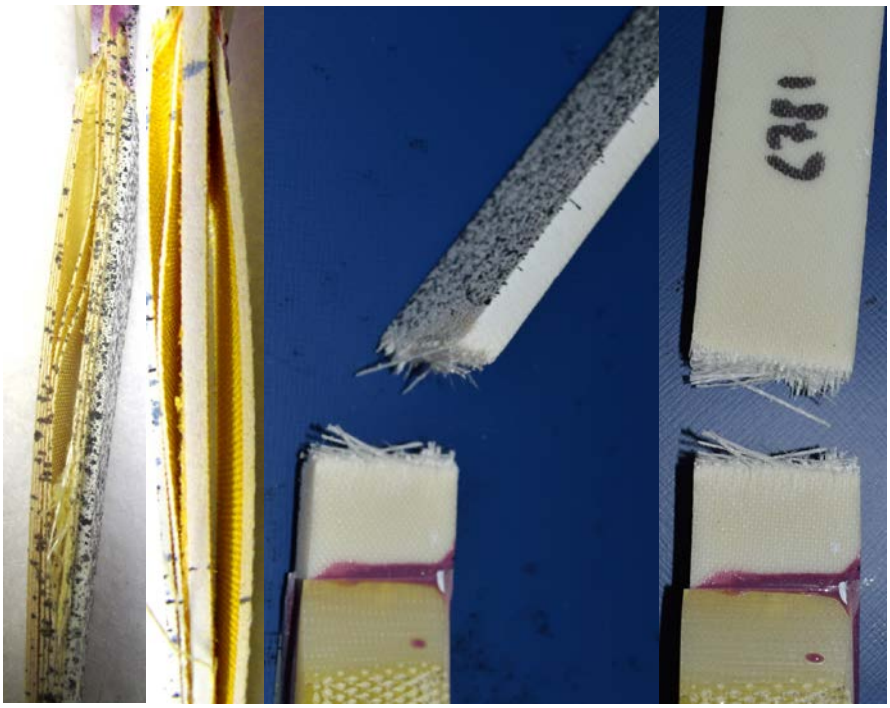

Fig. 6 Failure modes of satin-weave 6781 S2-glass composites with (left) p-DCPD matrix and (center and right) SC-15 matrix

The PPG E-glass, X1-glass and X2-glass, the biaxial stitched E-glass, and the AGY S2-glass demonstrated similar trends in tensile properties compared to the satin-weave composites. The PPG E-glass (washed) woven roving, the AGY S2-glass woven roving, and the biaxial stitched E-glass had both SC-15 and p-DCPD composites for direct comparison. The PPG E-glass composites has similar strength values but a significant drop in stiffness (about 25%). The AGY S2-glass–SC-15 composite had very similar stiffness and strength values to the other S2-glass composite (6781 satin weave); however, the AGY S2-glass with 933 sizing did not wet well with the p-DCPD resin and produced a composite with a large void-volume fraction of 7.6% (Table 2). As a result, under the tensile load, the AGY S2-glass–p-DCPD composite slipped in the grips and sheared off the top layers, producing no usable data. The biaxial E-glass composite tested successfully with both resins, and a 20% drop in stiffness and 10% drop in strength were observed for the p-DCPD resin composite. It is unclear whether the PPG 2026 sizing and/or the unidirectional tows of the biaxial stitched-fabric architecture contributed to an improved tensile performance of the biaxial E-glass–p-DCPD composite.

The PPG X1- and X2-fibers were infused with only p-DCPD resin, but still support the observed trend that p-DCPD matrix composites have decreased stiffness and strength in tension due to low interlaminar shear properties. A 25% increase in stiffness is observed between the PPG X1-fiber–p-DCPD composites, washed

versus unwashed; however, the strength values are roughly equivalent. Unlike the SBS data (Table 5), the tensile data could be indicating an advantage to removing the film former—known to be incompatible with the p-DCPD resin's chemistry—but this is unclear. The PPG X2-glass fiber with T-74 sizing was infused with 2 types of p-DCPD resin: Spencer Composites ESM-611+ and Telene p-DCPD. The ESM-611+ p-DCPD resin composite had a 10% decrease in modulus and a 42% increase in tensile strength over the Telene p-DCPD composite. As with the satin-weave p-DCPD composites, the failure modes demonstrated by the woven roving and biaxial stitched composites were gage-length delaminations indicating poor interlaminar shear strength (Fig. 7).

Fig. 7 Group of samples tested in tension: (left) biaxial stitched E-glass–p-DCPD, (center left) biaxial–SC-15, (center right) PPG X2-glass–Spencer p-DCPD, and (right) PPG X2-glass–Telene p-DCPD

3.2 Impact Testing

Low-velocity-impact testing was conducted on all of the composites listed in Table 4; a total of 5 samples. The data-acquisition system generates force-versus-time data during the 20 ms of the impact event. The force was integrated twice versus

time to calculate out-of-plane displacement or deflection. The force-deflection curves for all 4-quadrant impacts are then plotted for each material. Damage per impact was also tracked by performing through-thickness ultrasonic scanning after each impact. The images were analyzed subjectively to assess damage. Visual inspection of damaged panels (front/back, edges, and cut sections) was conducted to understand failure modes.

3.2.1 Force-Deflection Curves

Force-defection curves for each composite are presented in Figs. 8–12. Figures 8 and 9 represents the impact-stiffness behavior for PPG E-glass fabric with SC-15 resin and p-DCPD resin, respectively.

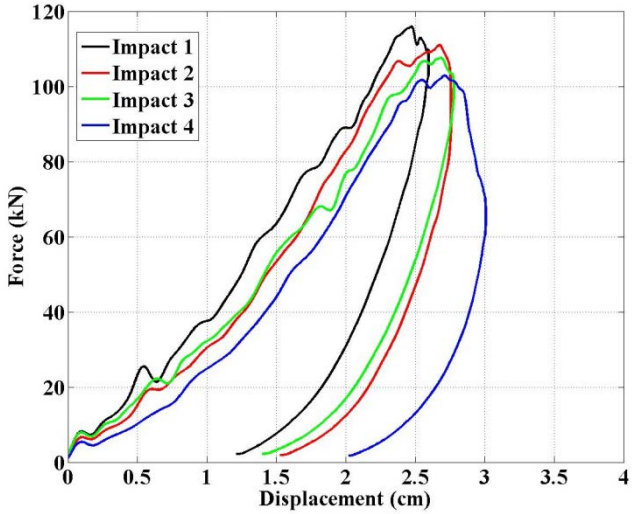

Fig. 8 Force-deflection curve for PPG E-glass–SC-15 processed with VARTM

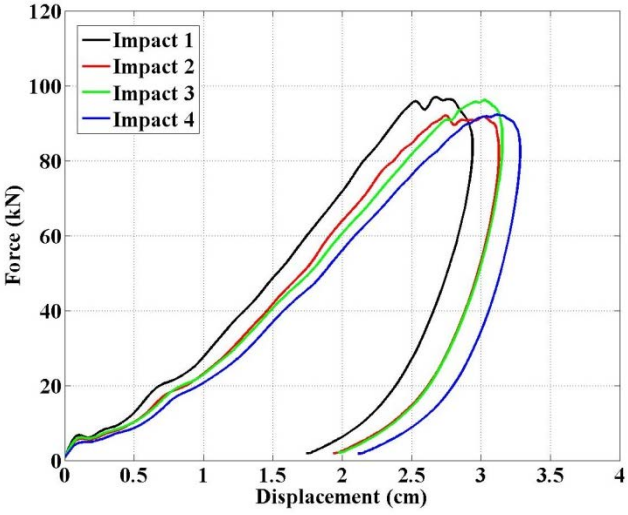

Fig. 9 Force-deflection curve for PPG E-glass–p-DCPD process with VARTM

Figures 10 and 11 represent the same composite subject although manufactured with PA-VARTM, which is designed to increase the fiber-volume fraction and mechanical performance of the composite.

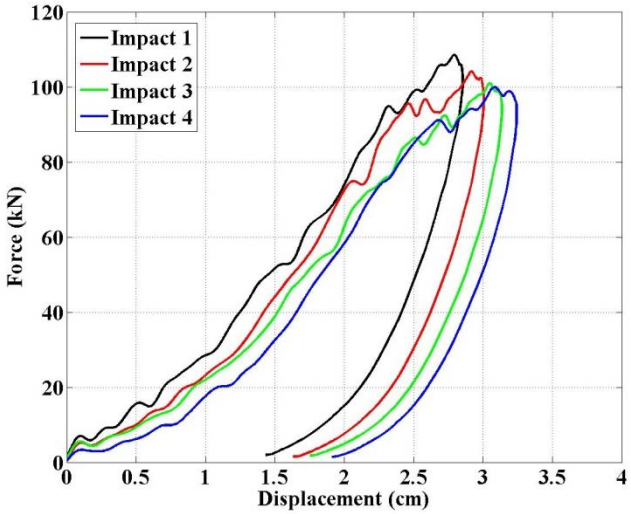

Fig. 10 Force-deflection curve for PPG E-glass–SC-15 processed using PA-VARTM

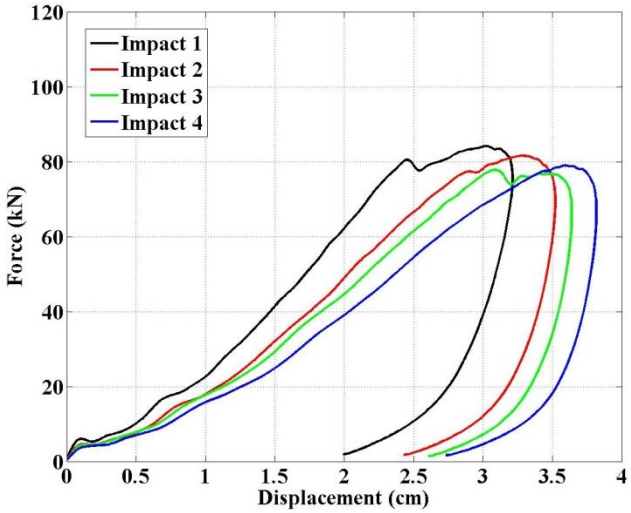

Fig. 11 Force-deflection curve for PPG E-glass–p-DCPD processed using PA-VARTM

Figure 12 represents the PPG X2-glass–Telene p-DCPD composite. The first 4 composites, in Figs. 8–11, were subjected to a 1.4-kJ impact energy due to the lower thicknesses and areal densities of the PPG E-glass composites (listed in Table 4); the thicker PPG X2-glass composite in Fig. 12 was subjected to a 2.1-kJ impact energy. (These impact energies were based on experience in tests whose goal was severe damage of the composites by the fourth impact.)

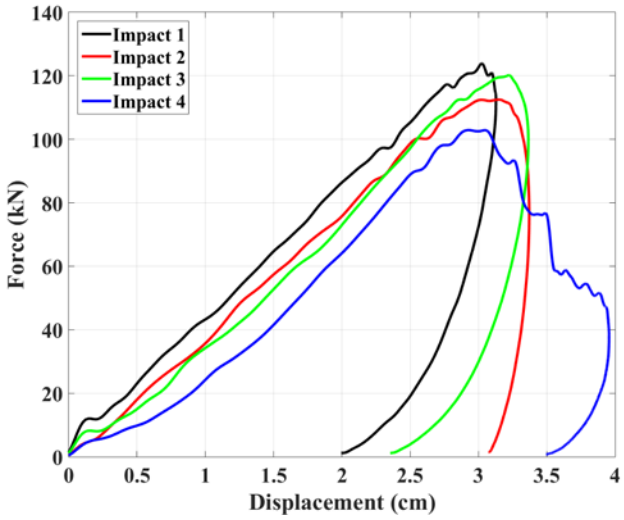

Fig. 12 Force-deflection curve for PPG X2-glass–Telene p-DCPD

The PPG E-glass–SC-15 composite of Fig. 8 has a peak load of approximately 120 kN with a maximum deflection of 3 cm by the fourth impact. The corresponding p-DCPD matrix composite of Fig. 9 has a lower peak load of 100 kN and a maximum deflection of more than 3 cm after Impact 1. The p-DCPD composite sustains more damage per impact and is intrinsically more compliant. At a deflection of 1 cm, the impact stiffness of the SC-15 resin composite is about 40 kN/cm versus less than 30 kN/cm for the p-DCPD resin composite. Figure 9 shows that the force-deflection curves for Impacts 2–4 are more tightly grouped. This is a strong indication the p-DCPD matrix composite is almost completely damaged after the first impact.

The PA-VARTM composites of Figs. 10 and 11 demonstrate similar trends. The PA-VARTM PPG E-glass–SC-15 composite of Fig. 10 has a slightly lower peak load of 110 kN (compared to regular VARTM processing) and increased deflection greater than 3 cm. This performance degradation is also observed in the corresponding p-DCPD composite although under the action of a different mechanism. The PA-VARTM SC-15 resin composite's impact performance is degraded probably due to the 3% fiber-volume increase rendering the composite stiffer under impact and more susceptible to multiple interlaminar delaminations. The PA-VARTM p-DCPD resin composite also exhibits degraded impact performance but, in contrast, likely due to an increase in the void content (4% versus 0.8%, according to Table 3). Indeed, the p-DCPD resin composite of Fig. 12 has a lower peak load of 80 kN and deflection greater than 3.5 cm. Again, after the first impact the panel is almost completely damaged.

The PPG X2-glass–Telene p-DCPD composite sample was impacted at 2.1 kJ due to its higher areal density. The force-deflection data are presented in Fig. 12. This

panel represents an attempt to apply a more chemically compatible sizing (T-74) for the p-DCPD resin to improve both mechanical and impact properties. The impact performance of the X2-glass fiber composite is comparable to impact data obtained for S2-glass–SC-15 composites as presented in the references for the 4-quadrant impact protocol.[19,20] The peak load of 120 kN and the stiffness degradation per impact is comparable; however, the Telene p-DCPD composite has a distinctly unique rebound behavior. The rebound parts of the curves are not grouped as in the other composites (Figs. 8–11). This strongly indicates the damage per impact is more localized with crushing under the impactor in contrast to delamination or crumpling, which may extend out to the edge beyond the vicinity of the impact. This localized crushing is especially apparent in Impact 4 in Fig. 12. This change in impact behavior, compared to the other impacted composites illustrated in the force-deflection curves, represents an improved impact response that constrains delamination and damage to the vicinity of the impact; it may indicate the T-74 sizing is improving the fiber–matrix bond and the interlaminar shear properties.

3.2.2 Damage Progression

During the evaluation of impact data it is important to look at the damage progression per impact in addition to force-deflection curves. Figures 13–17 are collective images taken after each impact on the 5 composites tested. Typically damage is indicated by dark blue with a lighter blue perimeter or a transition. A visual assessment of the figures reveals the p-DCPD resin composites (Figs. 14 and 16) performed quite poorly and showed excessive damage after each impact. Complete damage of the impact sample was observed after the second impact and the damage extended to the edges outside the impact aperture (inner square in the images). The SC-15 resin composites (Figs. 13 and 15) performed better, but were completely damaged after the third impact. Again, the composites processed using PA-VARTM showed more damage per impact, especially the p-DCPD resin composite (Fig. 16). The PPG X2-glass–Telene p-DCPD composite (Fig. 17) demonstrated a damage progression similar to the SC-15 composites (Figs. 13 and 15); again, another indication the T-74 sizing assisted in improving the interlaminar shearing strength of the p-DCPD composites.

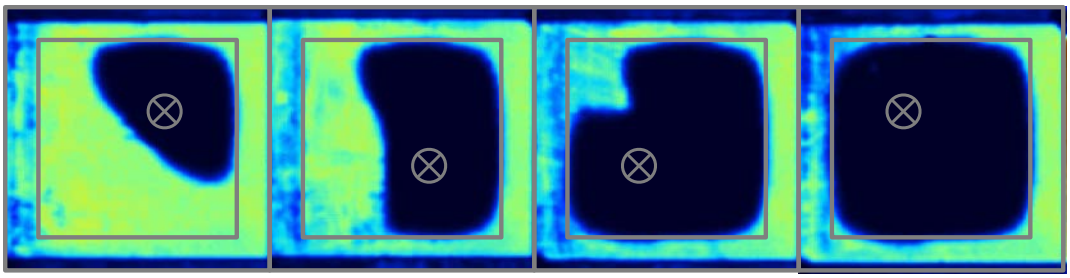

Fig. 13 Damage progression for PPG E-glass–SC-15 composite processed with VARTM

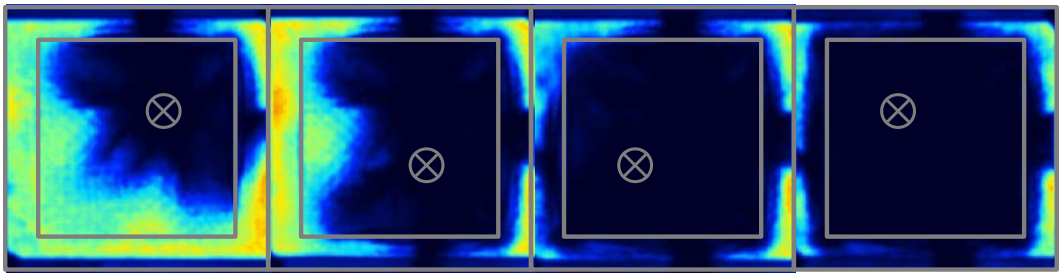

Fig. 14 Damage progression for PPG E-glass–p-DCPD composite process with VARTM

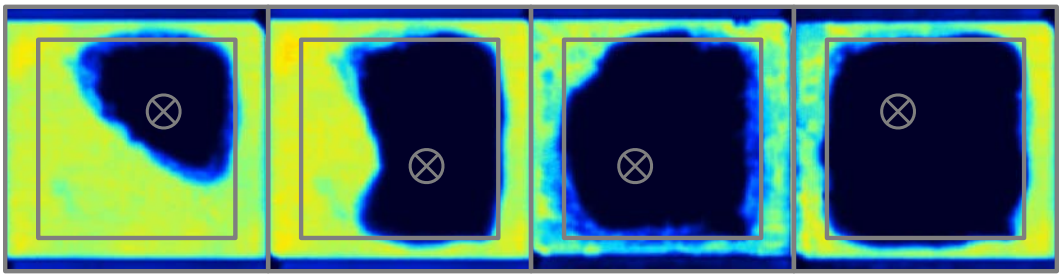

Fig. 15 Damage progression for PPG E-glass–SC-15 composite processed using PA-VARTM

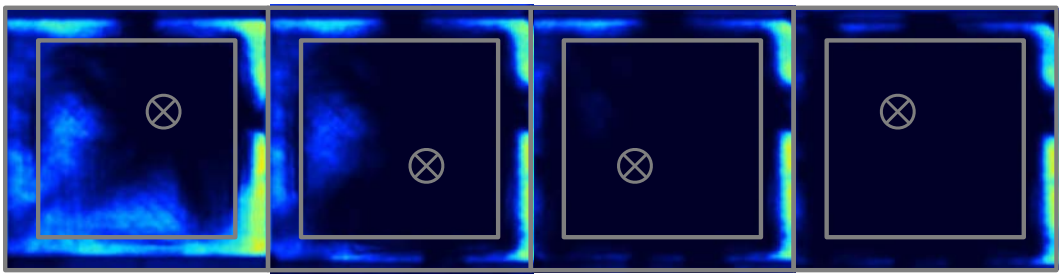

Fig. 16 Damage progression for PPG E-glass–p-DCPD composite processed using PA-VARTM

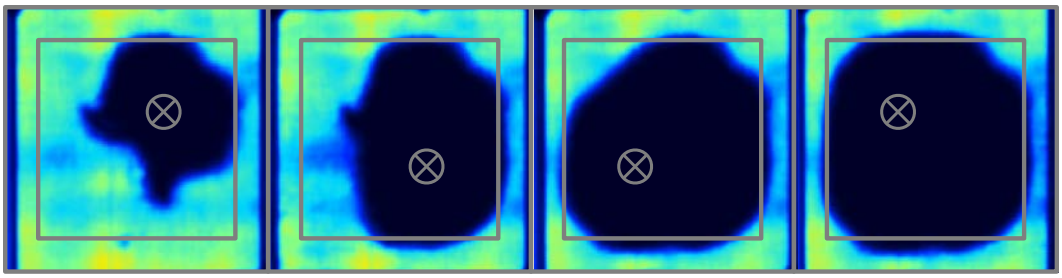

Fig. 17 Damage progression for PPG X2-glass–Telene p-DCPD composite

3.2.3 Damage Visualization

The ultrasonic scanning indicates only the presence and extent of damage and not the type. To properly determine the failure mode during the impact event, it is necessary to visually inspect the damaged composite or section through the damage to view the cross section. For impact, this damage is usually in the form of delamination planes between reinforcing layers of glass fabric, matrix cracking, impact puncture in the composite through multiple top layers, and/or kinking or crumpling extended to the edge. Each composite tested in impact was visually inspected in the vicinity of impact to note any distinct visible damage that would reveal the failure modes. A few composites were selected for sectioning through selected impact sites.

Front and back images of SC-15 and p-DCPD composites are presented in Figs. 18–20. Figure 18 compares the front-face impact damage of representative SC-15 and p-DCPD resin composites. The SC-15 shows much more surface damage in the vicinity of the 4 impacts than the p-DCPD; however, the p-DCPD resin composite has surface crumpled lines that extend out from the vicinity of the impact diagonally to the panel edge.

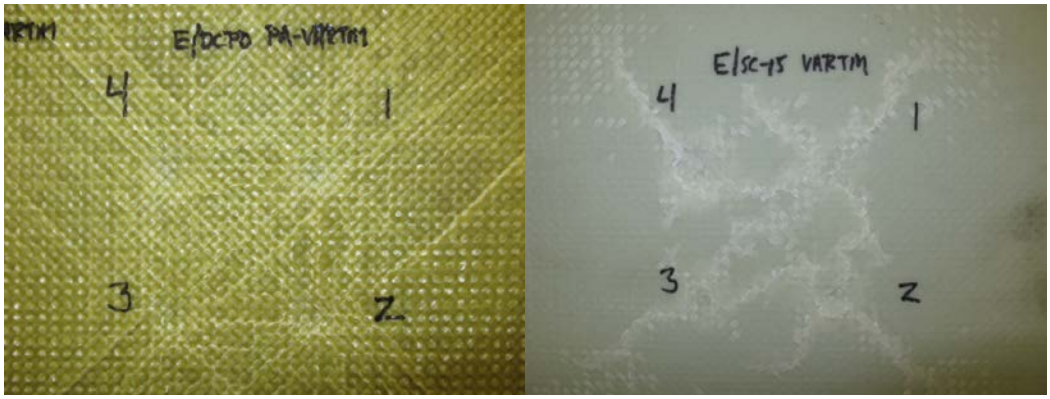

Fig. 18 Front-face damage for composites (left) PPG E-glass–p-DCPD and (right) PPG E-glass–SC-15

Fig. 19 Back-face damage for composites (left) PPG E-glass–SC-15 manufactured using standard VARTM and (right) PA-VARTM

Figure 19 gives back-face images of the 2 SC-15 resin composites allowing for an interesting contrast between standard VARTM- and PA-VARTM-manufactured panels. The PA-VARTM manufacturing process is typically used to improve the mechanical performance of the composite through increasing the fiber-volume fraction by about 2%–3%. The impact performance may be degraded for these composites due to an increase of the brittle fiber reinforcement at the expense of the ductile matrix. The standard VARTM panel displays 4 distinct back-face perforations with the fourth impact displaying the most damage, while the PA-VARTM panel has virtually no back-face perforations after the second impact. This difference was already noted and is supported by the force-deflection curves, Fig. 8 versus Fig. 10, and the progressive-damage scans of Figs. 13 and 15. The PA-VARTM panel absorbs impact energy through the formation of interlaminar delaminations that accumulate to render the panel more compliant under impact while the standard VARTM panel experiences more localized delaminations that result in more pronounced back-face perforations.

Figure 20 shows both front- and back-face images for the PPG X2-glass–Telene p-DCPD composite. This p-DCPD composite does not display the crumpled diagonal damage of the E-glass–p-DCPD composites but, rather, damage similar to the SC-15 resin composite. Damage is contained to the vicinity of the impact, especially for Impact 4, and there is no visual evidence of crumpling. Additional visual inspection of the edges of the p-DCPD resin composites reveals no edge kinking, which is representative of large-scale crumpling, as is observed in the 2 other PPG E-glass–p-DCPD composites (in Fig. 21). This further supports the observation that the T-74 sizing has improved the fiber–matrix bond and the interlaminar shear properties have improved impact performance.

Fig. 20 Front- (left) and back- (right) face damage for the PPG X2-glass–Telene p-DCPD composite

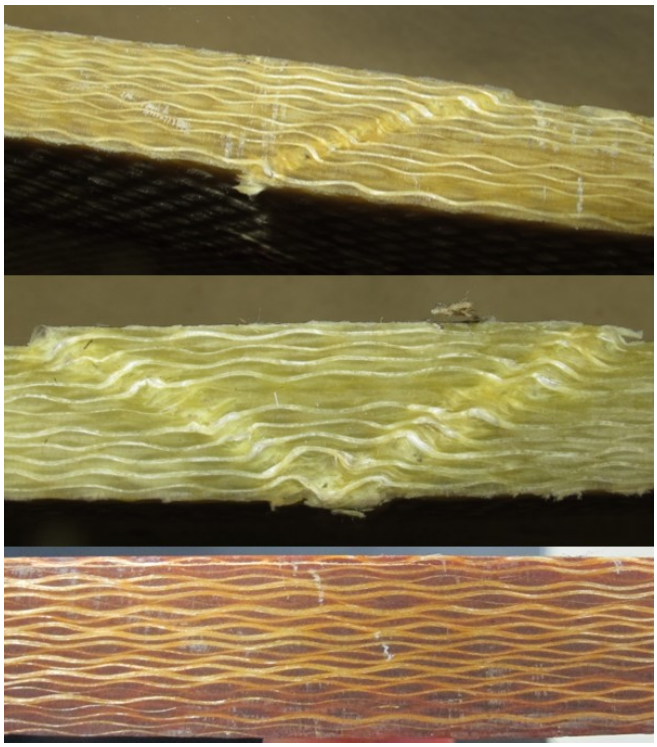

Fig. 21 Images of edge damage in p-DCPD composites subject to 4-quadrant impacts: (top) PPG E-glass–p-DCPD manufactured using standard VARTM, (center) same composite manufactured using PA-VARTM, and (bottom) PPG X2-glass–Telene p-DCPD

Sectioning through selected impact locations was also performed on all impact composites and dye applied to bring out damage on the cross sections. The lower-areal-density composites subjected to a 1.4-kJ impact energy were sectioned through Impacts 2 and 3; the thicker X2-glass composite subjected to 2.1 kJ was

sectioned through Impacts 3 and 4. Figure 22 shows the SC-15 resin composites (middle image) dissipate impact energy by developing large interlaminar delaminations that extend out significantly from the vicinity of the impacts. The p-DCPD, in contrast, absorbs the impact energy through significant permanent deformations under the impact (probably due to interlaminar matrix cracking) and whole-scale crumpling of the aperture of impact. As previously noted, the crumpling forms localized kinking fractures, which extend out to the edge of the panel. The PPG X2-glass–Telene p-DCPD composite, with improved interlaminar-shear properties, dissipates impact damage with localized punching damage under the impact and delaminations in the immediate vicinity of the 4 impacts.

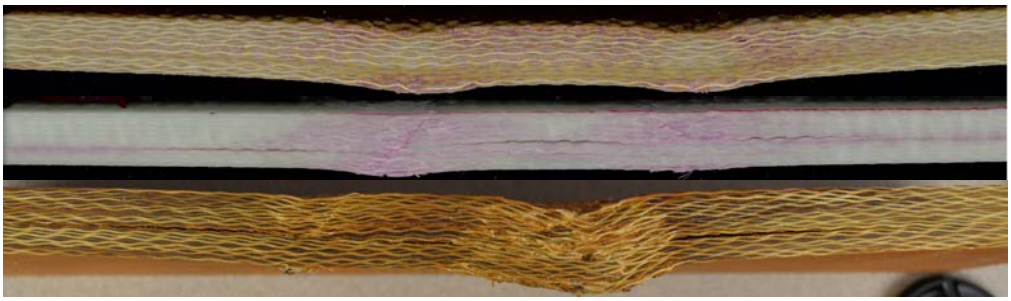

Fig. 22 Cross sections of 3 impacted composites: (top) PPG E-glass–p-DCPD, (center) PPG E-glass–SC-15, and (bottom) PPG X2-glass–Telene p-DCPD

4. Conclusion

Mechanical and impact testing were conducted on various SC-15 and p-DCPD resin composites to assess the suitability of the p-DCPD resin system as a viable replacement to traditional epoxies. Mechanical and impact testing conclusively identified p-DCPD composites' compromised mechanical and impact performance and properties compared to epoxy composites. The testing strongly indicates the culprit is low interlaminar strength due to poor adhesion and wetting at the fiber–matrix interface. Commercially available glass fabrics with epoxy-compatible sizings are not compatible with the p-DCPD's unique chemistry; moreover, p-DCPD composites processed with these sizings tend to have higher void-content fractions, unreacted resin at the fiber–matrix interface (as evidenced by a lingering odor after post-cure), and significantly compromised interfacial shear properties. Even though this was anticipated and an effort made to develop a more compatible sizing, the vinyl silane-based T-74 sizing on the X2-fibers was still not able to compete in mechanical and impact tests with the SC-15 epoxy-resin composites.

Most of the proprietary PPG sizings listed in Table 1 were optimized for ballistics impact using V_{50} testing[21] as the key metric. The requirements to improve ballistics performance are often contrary to improving structural response. A sizing must be

developed to allow the p-DCPD resin system to react fully at the fiber–matrix interface and form a strong bond. Optimizing this interface should maximize the shear-strength properties and improve interlaminar properties and structural performance. A program to develop chemically compatible sizings for the p-DCPD resin system with air-stable Ru catalyst is currently underway at ARL.

5. References

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List of Symbols, Abbreviations, and Acronyms

2-D	2-dimensional
AGY	Advanced Glassfiber Yarns
ARL	US Army Research Laboratory
ASTM	American Society for Testing and Materials
cP	centipoise
DIC	digital-image correlation
NA	not applicable
NC	not completed
PA-VARTM	press-assisted vacuum assisted resin transfer molding
p-DCPD	polydicyclopentadiene
PPG	Pittsburgh Plate Glass
ROMP	ring-opening metathesis polymerization
Ru	ruthenium
SBS	short beam shear
Tg	glass transition temperature
VARTM	vacuum-assisted resin transfer molding
V_f	volume, fibers
V_m	volume, matrix
V_v	volume, voids

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